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Laser ablation analysis of bivalve shells – archives of environmental information

Maiken Hansen Klünder, Dorothee Hippler, Rob Witbaard and Dirk Frei

Reconstructing past secular environmental variations is an important issue in palaeoclimate research. However, most key variables for palaeoclimate reconstructions cannot be measured directly, and reconstructions are therefore based on proxy data. Here, we demonstrate the potential of bivalve shells as an archive of environmental parameters. The Geological Survey of Denmark and Greenland (GEUS) has developed a fast and reliable method for chemical analyses of shell material by laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS), and here we present some examples of the use of this method.

In tropical and subtropical waters, corals can provide century-long archives of past water chemistry with annual resolution. A comparable archive for temperate and Arctic waters would be highly useful in climate research, and therefore it has been examined whether this can be provided by bivalve shells (e.g. Schoene *et al.* 2005). Long-lived species may provide archives with annual resolution extending over several hundred years, whereas short-lived, fast-growing species can provide archives with a seasonal or in some cases daily resolution over a period of a few years. Most bivalves are sessile, and shells are commonly preserved as fossils. There are, however, a number of challenges related to the use of bivalves as proxy archives: (1) many proxies show species specific behaviour (Seed 1980); (2) only very few proxies are dependent on a single variable (Wefer *et al.* 1999); and (3) the effects of biology and ontogeny on the uptake of trace elements and stable isotope fractionation in shell carbonate are largely unknown and have to be evaluated empirically. Therefore, any potential proxy must be calibrated individually for each species of interest before it can be used. A large number of chemical analyses are needed to calibrate a proxy. These are commonly obtained by solution ICP-MS, in which sample preparation is time-consuming and labour-intensive. The use of LA-ICP-MS is therefore a considerable advance in bivalve shell proxy research, as it greatly reduces the effort needed for sample preparation. At the same time, the method requires less material for analysis, thus providing better spatial and hence temporal resolution.

Proxies based on bivalve shell carbonate can be used in present-day environmental monitoring, and for environmental reconstructions from shells found as fossils. Shells from museum collections and shells found in archaeological mid-

dens can give information on historic and prehistoric environmental conditions (e.g. Carrell *et al.* 1987), and fossil shells can be used as archives of environmental parameters on geological timescales (e.g. Hendry *et al.* 2001).

Shell mineralisation

Bivalve shells consist mainly of calcium carbonate with impurities in the form of various elements substituting for calcium in the crystal structure. Calcium carbonate represents 95–99% by weight of the shell, the remaining 1–5% being organic matrix, which is dominated by proteins (Marin & Luquet 2004). The shell material is deposited sequentially in growth increments that are often visible in polished sections studied by computer-controlled scanning electron microscopy (CCSEM). As a consequence of the growth pattern the increments occur in chronological order, and a relative time line for chemical analyses can be established. A section with the different layers of the shell of the common blue mussel (*Mytilus edulis*) is shown in Fig. 1, where internal growth increments are also illustrated. Figure 2 shows an image of the actual shell structure.

The elements needed for shell mineralisation come from the water or from particles that the bivalve ingests. In order to be included in the shell, the elements have to cross two biological membranes, the outer and inner mantle epithelium. These membranes actively discriminate against certain elements, but for some elements this discrimination is influenced by external stimuli (e.g. Klein *et al.* 1996).

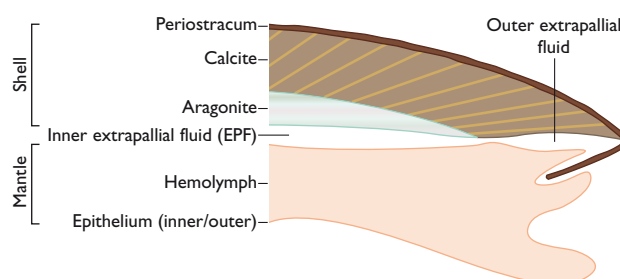


Fig. 1. Section through the margin of shell and mantle of a *Mytilus edulis*. The crystalline shell consists of two separate layers: a prismatic layer of calcite and an aragonitic layer of nacre. The outermost layer is a protective organic layer (periostracum). The shell is secreted in growth increments in the area between the shell and the mantle.

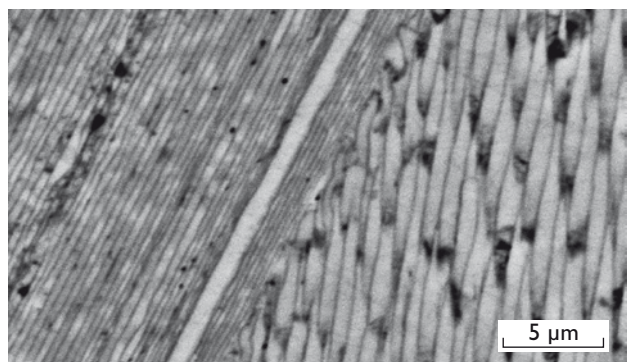


Fig. 2. SEM image of a *Mytilus edulis* shell in cross-section, showing aragonitic nacre (left side of image) and prismatic calcite (right side of image). The image illustrates the differences in structure between these two shell layers, and the direction of the growth increments.

The LA-ICP-MS method

Many previous studies of bivalve shells have utilised wet chemical analysis. Samples often consist of powder drilled from the shell with dentist drills and other microdrilling tools. Powder samples are routinely analysed by solution ICP-MS. LA-ICP-MS combines an analytical precision comparable to that of solution ICP-MS with a significantly shorter and easier sample preparation process. The laser technique is not only time-saving – the fewer steps needed in sample preparation also reduce the risk of contamination. Furthermore, the spatial resolution is much higher, as laser ablation in shell samples can be undertaken with a beam diameter of 30–65 μm , as opposed to the 200–300 μm diameter of a microdrill.

Sample preparation

Any sample of bivalve shell material can be analysed by LA-ICP-MS, but cross-sections through entire valves are preferred in order to constrain the growth history. The shell must be cleaned of soft tissues, epibionts or adhering sediment. The shell material is embedded in epoxy resin to prevent it from fracturing during handling. The shell is then cut with a diamond-tipped rock saw to produce a cross-section, and polished to show the shell structure (Fig. 3). Shells longer than 5 cm may have to be divided into two or more sections to fit into the sample chamber of commercially available laser ablation systems. After polishing, the section is cleaned with alcohol and treated ultrasonically to remove possible surface contamination.

Analytical techniques

The LA-ICP-MS equipment at GEUS is a Finnigan Element2 high resolution ICP-MS connected to a new wave

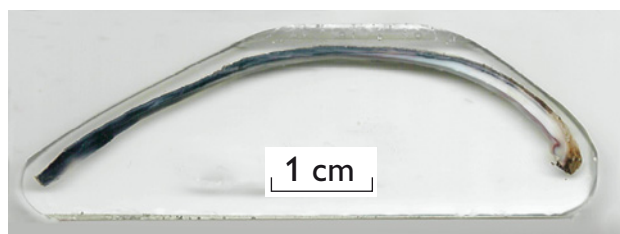


Fig. 3. Computer scan of shell sample *Mytilus edulis* B218 prepared for LA-ICP-MS analysis.

research UP213 laser ablation system. For shell analyses, the NIST 612 and NIST 614 glasses are used as standard materials. The elemental concentrations for the standard glasses published by Pearce *et al.* (1997) are used for concentration calculations. There are potential problems in using non-matrix-matched standards, but at ablation times of less than 80 seconds, these problems are not significant in analyses carried out on calcium carbonate (Vander Putten *et al.* 1999). As an internal standard in the samples, calcium (^{43}Ca) is suitable for the measurement of several trace and minor elements in calcite (Longerich *et al.* 1996), and SEM analyses of *M. edulis* have shown that the calcium content in the calcite layer is uniform. We use the Glitter software package for final concentration calculations from the time-resolved raw data.

Relative age and growth rate

An advantage of calibrating a proxy on bivalve shells taken from laboratory or field culturing experiments is that measurements of the shell length can be made during the experiment, so that the chemical analyses can be time constrained. When applying the proxy to fossil shells, it is of course impossible to carry out multiple shell length measurements on the live individual, so other methods must be used. Many species form annual growth increments that can be used to set the relative age of a specimen. Furthermore, all species show micro-increments that are visible in a microscope. These narrow growth increments are not always regular, but in a number of species the increments show a periodicity related to moon phases or diurnal or tidal shifts. Utilising what is known about the periodicity of increment formation in the species analysed, one can assign relative ages to chemical analyses and calculate approximate growth rates for the analysed shell.

Examples

Mg/Ca thermometry

The use of the ratio between Mg and Ca in shells as a temperature proxy was first suggested because it was found that the Mg/Ca ratio in marine carbonates varies according to lat-

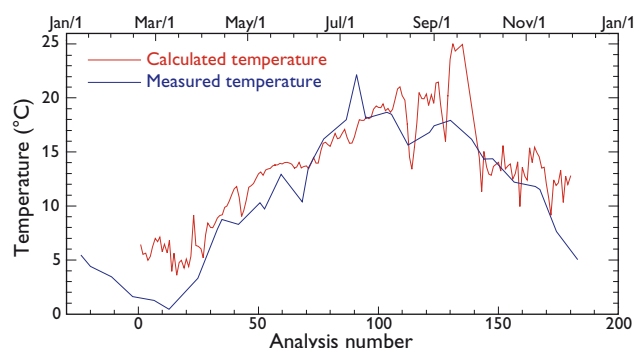


Fig. 4. Temperatures in Svendborg Sund, Denmark in the summer of 2005 calculated from Mg/Ca ratios in *Mytilus edulis* (red line) and compared to measured water temperatures (blue line). The calculated temperatures provide a fair estimate of the actual temperature.

itude (see Henderson 2002). Using calcite from *M. edulis* taken from field culturing experiments in the Wadden Sea, we found shell Mg/Ca ratios to be temperature dependent. The Mg/Ca ratio of *M. edulis* shells from Svendborg Sund, Denmark was then used to calculate seawater temperatures. The temperature was calculated from the Mg/Ca ratio using the equation $T = 2.22 + 18.2 \log (\text{Mg/Ca})$ (unpublished data, M.H. Klünder). The calculated temperatures have been compared with water temperatures measured by the National Environmental Research Institute (Fig. 4). It is seen that the Mg/Ca thermometer gives a fair estimate of temperature changes during a summer.

Lead pollution

The concentration of Pb in shell increments of the bivalve *Mya arenaria* is a function of the Pb concentration in the water (Pitts & Wallace 1994), and hence the former concentration of Pb in the water can be calculated from the lead concentration in *M. arenaria* shells. Shell samples from a four-year old specimen from Limfjorden, Denmark, collected in

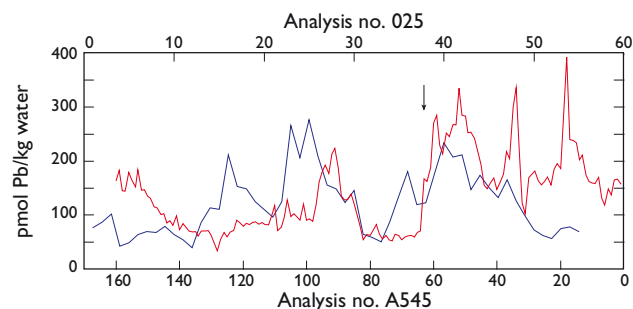


Fig. 5. Pb content in seawater calculated from shell Pb concentration using the equation of Pitts & Wallace (1994). One specimen of *Mya arenaria* (blue line, Limfjorden) and one specimen of *Arctica islandica* (red line, Baltic Sea, transplanted to the Netherlands) were analysed. The arrow shows the time of the transplantation.

2005, have been analysed. The results indicate that the Pb concentration in Limfjorden has varied from 20 to 280 pmol/kg water over the sampled time span (Fig. 5). Hence analysing a single water sample may give a misleading picture of the Pb level. The concentration of Pb in Limfjorden is comparable to that found in the relatively uncontaminated Cape Cod Bay, eastern USA; it is up to ten times higher than pre-industrial levels in the Boston area, as calculated from the Pb content of sub-fossil shells from shell middens, and ten times lower than in Boston harbour (Pitts & Wallace 1994).

The Pb proxy has also been applied to data from an *Arctica islandica* individual that was transferred from the Baltic Sea to a Dutch harbour (Fig. 5). The proxy has not yet been calibrated for *A. islandica*, and the results can only be regarded as qualitative. However, it is seen that the Pb concentration in shell material secreted after transplantation to the harbour is significantly higher than in that secreted in the Baltic. These results indicate that shells of *A. islandica* can be used to monitor Pb contamination of seawater.

Shell Mn/Ca and Ba/Ca – a link to primary production?

It has been suggested that the content of Mn and/or Ba in bivalve shells can be correlated with primary production (e.g. Stecher *et al.* 1996). This would suggest that Mn/Ca or Ba/Ca ratios are related to phytoplankton blooms, providing a proxy

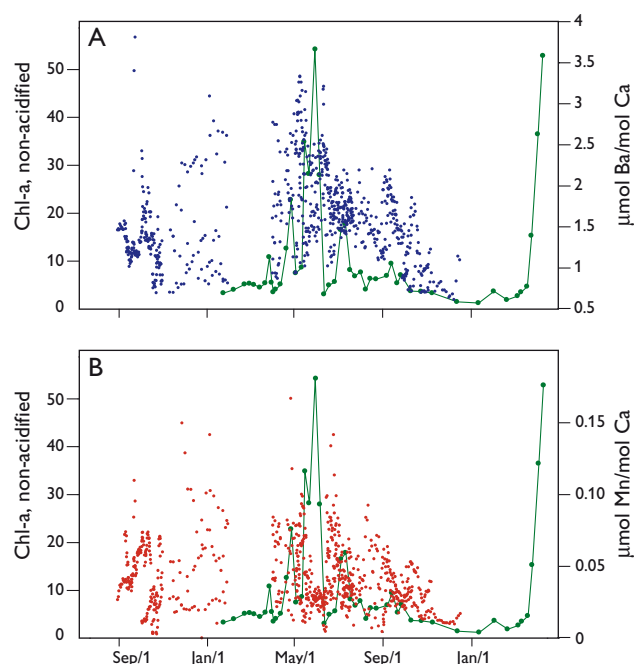


Fig. 6. Ba/Ca and Mn/Ca ratios of four *Mytilus edulis* specimens compared with the chlorophyll-a concentrations (red line) of the seawater. **A:** Ba/Ca ratios in *M. edulis* shells from the Dutch Wadden Sea. **B:** Mn/Ca measured in the same shells.

for the timing and size of such events. To test this theory, *M. edulis* shell samples from an aquaculture field experiment site in the Wadden Sea were analysed at GEUS and compared to the chlorophyll-a concentration of the ambient water (Fig. 6). The results are not conclusive, but they suggest that the relationships between the Mn/Ca or Ba/Ca ratios and the chlorophyll-a concentration are not simple linear functions. The Ba/Ca ratio in the shells seems to increase with the chlorophyll-a concentration in the water, but continues to remain at an elevated level after the end of the bloom; however, Mn/Ca seems to have a correspondence with the peaks of some less intensive algae blooms, but is quite low during the most pronounced bloom recorded in May. Clearly, further research is needed to better understand the link between Mn/Ca and Ba/Ca ratios in shell material and phytoplankton blooms.

Final remarks

The LA-ICP-MS method is a reliable and advantageous technique for the analysis of a wide range of trace elements in carbonates. The combination of relatively high precision, low detection limits, high spatial resolution, straightforward sample preparation and fast analysis makes the method especially suited for research and application of calcium carbonate based proxies. Further development of biogenic carbonate proxies will have benefits for both palaeo-climate research and investigation into the processes of biomineralisation, as well as for environmental studies.

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Authors' addresses

M.H.K. & D.F., *Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark*. E-mail: mbk@geus.dk
D.H., *Faculty of Earth and Life Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, the Netherlands*.
R.W., *Royal Netherlands Institute for Sea Research (NIOZ), P.O. Box 59, 1790 AB Den Burg (Texel), the Netherlands*.